

TITLE: Water Gas Shift Kinetics at Membrane Reactor Conditions

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### **ABSTRACT**

Water-gas shift is an old and established technology that may find new applications in fuel cell and coal processing systems. Water-gas shift is a reversible, exothermic reaction that is thermodynamically unfavorable at elevated temperatures. Membrane reactors have been identified as a potentially beneficial technology for use in these new applications of water-gas shift. By combining the reaction with selective removal of one of the reaction products, a single reactor can operate simultaneously at high temperature and high conversion. Conceptually, such a reactor could use a membrane that is highly permselective for either  $H_2$  or  $CO_2$ .

The conditions for water gas shift in a membrane reactor would be very different from those encountered in a conventional shift reactor. In a conventional shift reactor, excess steam is used to drive the reaction thermodynamically. In contrast, a membrane reactor would likely use a more nearly stoichiometric feed, and at the desired high conversions, the gas phase would be predominantly either  $CO_2$  or  $H_2$ , whichever was not removed through the membrane. The first part of this project has involved studying the kinetics of water gas shift with an emphasis on these conditions. The experimental results have been combined with published data for conditions more typical of a present-day commercial water gas shift reactor and used to develop a microkinetic model for water gas shift over commercial type iron oxide catalysts. The resulting kinetic model has been incorporated into a membrane reactor model to allow assessment of catalyst performance along with its impact upon critical membrane reactor design parameters. In particular, this kind of model can be used to determine the relative extent to which chemical reaction and membrane permeation are limiting the performance of the reactor.

In situations where carbon dioxide is selectively removed, the partial pressure of hydrogen will build as conversion increases. The experimental studies showed that hydrogen partial pressures above a critical limit lead to a change in the catalyst and an onset of undesired reactions. Specifically it appears that the catalyst is reduced to metallic iron and Fischer-Tropsch chemistry begins to take place. In situations where hydrogen is selectively removed, carbon dioxide partial pressure will build as conversion increases. The kinetic measurements confirmed previous studies showing strong inhibition of the rate by carbon dioxide. For example, if a membrane reactor operates at a reaction pressure of 1000 psia and at 733 K, with 95% recovery of hydrogen, by 90% conversion, the rate of reaction will have decreased by over three orders of magnitude over this range of conversion.

The microkinetic model was used to explore whether the catalyst might be modified so that it would be less susceptible to inhibition by  $\text{CO}_2$ . The model predicts that weakening the bond strength of surface oxygen will lessen the degree of inhibition by carbon dioxide. That is, modifications that render the catalyst more easily reducible are predicted to also lessen the degree of inhibition by  $\text{CO}_2$ . Furthermore, recent literature suggests that the addition of ceria to the catalyst formulation leads to a lowering of the onset temperature for catalyst reduction. Consequently, ceria-promoted iron oxide catalysts were prepared and evaluated kinetically. The inhibition of water gas shift by  $\text{CO}_2$  over these promoted catalysts was equal to the inhibition over the unpromoted catalyst. At present, it is not clear whether the microkinetic model is inaccurate, whether the report is incorrect that ceria-promoted catalysts are more easily reducible, or whether our particular formulation somehow differed from the one reported to be more reducible. Studies are presently underway to compare the reducibility of our promoted and unpromoted catalysts.

A survey of other reportedly active water gas shift catalysts has also been undertaken. In particular, the so-called sulfur tolerant shift catalysts may prove to be attractive. These catalysts are very similar to HDS catalysts; they are sulfides in their active state. Three features of these catalysts may be important. First, they are active at lower temperatures than iron oxide catalysts; this may be important if facilitated transport types of membranes are employed because the latter can't operate at elevated temperatures. In addition, since these catalysts are sulfides and require a sulfur source in the feed, they will not be susceptible to the reduction experienced by the iron oxides at high hydrogen partial pressures. It also appears that these catalysts are less severely inhibited by  $\text{CO}_2$  than iron oxides. We are presently using microkinetic models we developed previously for sulfur tolerant water gas shift catalysts, in combination with membrane reactor models, to assess the performance of this class of catalysts at membrane reactor conditions.